

(12) UK Patent Application

GB (19) 2 248 068 (13) A

(43) Date of A publication 25.03.1992

(21) Application No 9020604.6	(51) INT CL ⁶ C10M 129/26
(22) Date of filing 21.09.1990	(52) UK CL (Edition K) C5G GAB G135 G140A G162
(71) Applicant Exxon Chemical Patents, Inc (Incorporated in the USA - Delaware) 200 Park Avenue, Florham Park, New Jersey 07932, United States of America	(56) Documents cited GB 2118061 A GB 2092016 A GB 2085314 A GB 2043481 A GB 1579001 A GB 1565000 A GB 0966882 A EP 0058330 A1
(72) Inventors Michael David Sexton Anthony Kitson Smith	(58) Field of search UK CL (Edition K) B1E, C5G GAA GAB INT CL ⁶ C10M Online databases: WPI; CLAIMS
(74) Agent and/or Address for Service Abel & Imray Northumberland House, 303-306 High Holborn, London, WC1V 7LH, United Kingdom	

(54) Oil compositions and novel additives

(57) An additive for reducing smoke and particulate emissions during combustion of a fuel oil, especially diesel fuel, comprises a novel composition of

- (a) a compound of an alkali metal
- (b) a compound of a metal of group 2a of the Periodic Table and
- (c) a compound of a transition metal selected from groups 1b, 3b, 4b, 5b, 6b, 7b and 8 of the Periodic Table.

GB 2 248 068 A

- 1 -

"Oil Compositions and Additives"

This invention relates to oil compositions, and to additives for use in such compositions. More especially it relates to fuel oil, especially diesel, heating, and jet, fuel oil compositions, and to reduction of smoke and particulate emissions on combustion.

Although modern internal combustion engines are highly efficient and give almost complete combustion of the hydrocarbon fuel used, the slight reduction from total efficiency leads to the formation of black smoke, a proportion of which is particulate carbon. Apart from the smoke's being unpleasant to breathe and unsightly, the carbon particles may have absorbed in them polynuclear hydrocarbons, also resulting from incomplete combustion. Some of these hydrocarbons are known carcinogens.

It has previously been proposed to reduce the emission of particulates by incorporating in the fuel one or more additives which improve combustion efficiency by some means. Numerous patent publications describe the use of an alkaline earth or alkali metal additive to reduce smoke emission, and some of these describe the use of such an additive with a transition metal additive for such purposes. Further patent publications describe combinations of different metal additives for use in other hydrocarbon fluids, e.g., lubricating oils and gasolines, and in fuel oils for purposes other than inhibiting smoke emission. Among these publications

there may be mentioned WO 87/01126 and WO 88/03144, and British Specification No. 1413902.

The present invention provides a composition for use as a fuel oil additive for the inhibition of smoke and/or particulate emissions on combustion of the oil, which composition comprises:

- (a) a compound of an alkali metal,
- (b) a compound of a metal of group 2a of the Periodic Table, and
- (c) a compound of a transition metal selected from Groups 1b, 3b, 4b, 5b, 6b, 7b or 8 of the Periodic Table.

It is within the scope of the invention for the additive composition to comprise two or more compounds in any of categories (a), (b) and (c), and such compounds may be of the same or of different metals.

The version of the Periodic Table used in this specification is that published in the Handbook of Chemistry and Physics, 57th Edition, CRC Press, Inc.

Among alkali metals there may be used advantageously, lithium and, preferably, sodium and potassium.

Among Group 2a there may be used, advantageously, magnesium, strontium, and, preferably, calcium and barium.

Among the transition metals there may be used technetium and, advantageously, scandium, titanium,

vanadium, yttrium, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, hafnium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold, a lanthanide, and, preferably, chromium, manganese, iron, cobalt, nickel, copper, and lanthanum.

Particularly preferred combinations are compounds of sodium or potassium; barium or calcium; and cobalt or iron.

The type of metal compound is not important provided that the combination of compounds making up the additive is soluble in the fuel oil in which it is to be used at the concentration in which it is to be used. This is conveniently achieved by using the metals in the form of salts of organic acids. As examples of organic acids, there may be mentioned carboxylic acids and their anhydrides, phenols, sulphurized phenols, and sulphonated acids.

The carboxylic acid may be, for example:

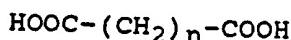
- i) An acid of the formula:



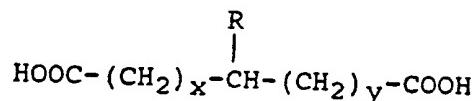
where R is hydrogen, or a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, cycloalkenyl, or aryl group. Examples of such acids include formic acid, acetic acid, propionic acid, butyric acid, valeric acid, palmitic acid, stearic acid, cyclohexanecarboxylic acid, 2-methylcyclohexane carboxylic acid, 4-methylcyclohexane carboxylic acid, oleic acid, linoleic acid, linolenic

acid, cyclohex-2-eneoic acid, benzoic acid, 2-methylbenzoic acid, 3-methylbenzoic acid, 4-methylbenzoic acid, salicylic acid, 2-hydroxy-4-methylbenzoic acid, 2-hydroxy-4-ethylbenzoic acid, p-hydroxybenzoic acid, 3,5-di-tert-butyl-4-hydroxybenzoic acid, o-aminobenzoic acid, p-aminobenzoic acid, o-methoxybenzoic acid and p-methoxybenzoic acid.

ii) A dicarboxylic acid of the formula



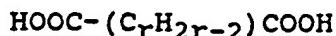
where n is zero or an integer, including e.g. oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid and suberic acid. Also included are acids of the formula



where x is zero or an integer, y is zero or an integer and x and y may be equal or different and R is defined as in (i). Examples of such acids include the alkyl or alkenyl succinic acids, 2-methylbutanedioic acid, 2-ethylpentanedioic acid, 2-n-dodecylbutanedioic acid, 2-n-dodecenylbutanedioic acid, 2-phenylbutanedioic acid, and 2-(p-methylphenyl)butanedioic acid. Also included are polysubstituted alkyl dicarboxylic acids wherein other R groups as described above may be substituted on the alkyl chain. These other groups may be substituted on the same carbon atom or different atoms. Such examples include 2,2-dimethylbutanedioic acid;

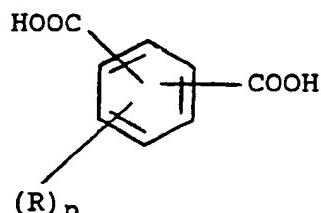
2,3-dimethylbutanedioic acid; 2,3,4-trimethylpentanedioic acid; 2,2,3-trimethylpentanedioic acid; and 2-ethyl-3-methylbutanedioic acid.

The dicarboxylic acids also include acids of the formula:



where r is an integer of 2 or more. Examples include maleic acid, fumaric acid, pent-2-enedioic acid, hex-2-enedioic acid; hex-3-enedioic acid, 5-methylhex-2-enedioic acid; 2,3-di-methylpent-2-enedioic acid; 2-methylbut-2-enedioic acid; 2-dodecylbut-2-enedioic acid; and 2-polyisobutylbut-2-enedioic acid.

The dicarboxylic acids also include aromatic dicarboxylic acids e.g. phthalic acid, isophthalic acid, terephthalic acid and substituted phthalic acids of the formula:



where R is defined as in (i) and n = 1, 2, 3 or 4 and when n > 1 then the R groups may be the same or different. Examples of such acids include 3-methylbenzene-1,2-dicarboxylic acid; 4-phenylbenzene-1,3-dicarboxylic acid; 2-(1-propenyl)benzene-1,4-dicarboxylic acid, and 3,4-dimethylbenzene-1,2-dicarboxylic acid.

The carboxylic acid anhydrides include the anhydrides that may be derived from the carboxylic acids described above. Also included are the anhydrides that may be derived from a mixture of any of the carboxylic acids described above. Specific examples include acetic anhydride, propionic anhydride, benzoic anhydride, maleic anhydride, succinic anhydride, dodecylsuccinic anhydride, dodecenylsuccinic anhydride, an optionally substituted polyisobutylenesuccinic anhydride, advantageously one having a molecular weight of between 500 and 2000 daltons, phthalic anhydride and 4-methylphthalic anhydride.

The phenols from which the anion may be derived are of many different types. Examples of suitable phenols include:

(i) Phenols of the formula:

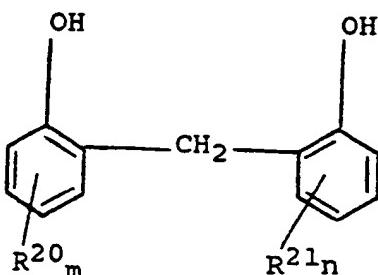


where $n = 1, 2, 3, 4$ or 5 , where R^{20} is defined below and when $n > 1$ then the substituents may be the same or different. R^{20} may be hydrogen, or a substituted or unsubstituted, alkyl, cycloalkyl, alkenyl, cycloalkenyl or aryl group. The hydrocarbon group(s) may be bonded to the benzene ring by a keto or thio-keto group.

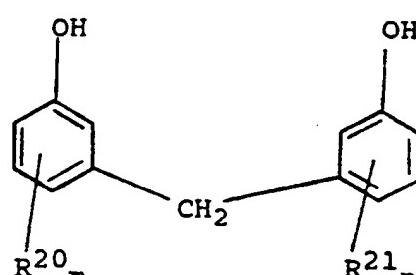
Alternatively the hydrocarbon group(s) may be bonded through an oxygen, sulphur or nitrogen atom. Examples of

such phenols include o-cresol; m-cresol; p-cresol; 2,3-dimethylphenol; 2,4-dimethylphenol; 2,3,4-trimethylphenol; 3-ethyl-2,4-dimethylphenol; 2,3,4,5-tetramethylphenol; 4-ethyl-2,3,5,6-tetramethylphenol; 2-ethylphenol; 3-ethylphenol; 4-ethylphenyl; 2-n-propylphenol; 2-isopropylphenol; 4-isopropylphenol; 4-n-butylphenol; 4-isobutylphenol; 4-sec-butylphenol; 4-t-butylphenol; 4-nonylphenol; 2-dodecylphenol; 4-dodecylphenol; 4-octadecylphenol; 2-cyclohexylphenol; 4-cyclohexylphenol; 2-allylphenol; 4-allylphenol; 2-hydroxydiphenyl; 4-hydroxydiphenol; 4-methyl-4'-hydroxydiphenyl; o-methoxyphenol; p-methoxyphenol; p-phenoxyphenol; 2-hydroxydiphenylsulphide; 4-hydroxydiphenylsulphide; 4-hydroxyphenylmethylsulphide; and 4-hydroxyphenyldimethylamine. Also included are alkyl phenols where the alkyl group is obtained by polymerization of a low molecular weight olefin e.g. polypropylphenol or polyisobutylphenol.

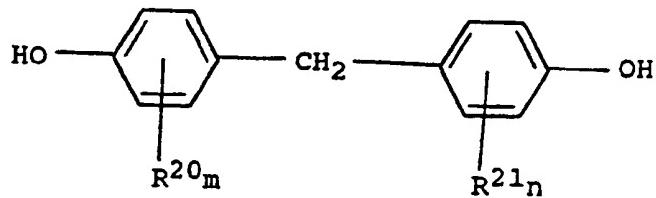
Also included are phenols of the formula:



and/or

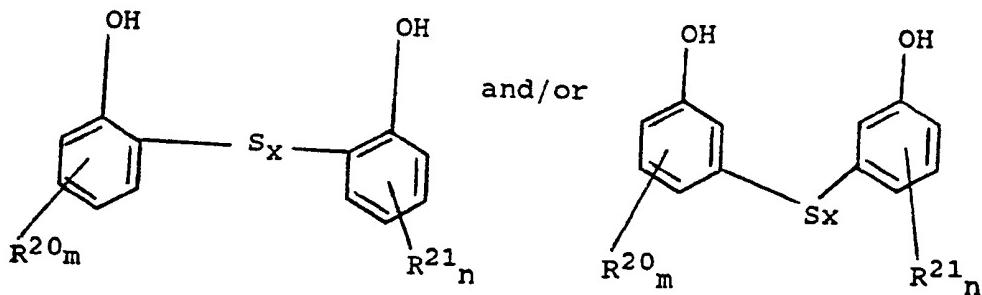


and/or

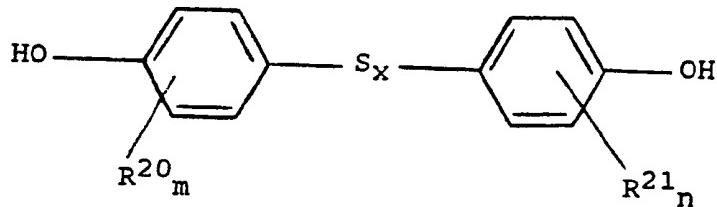


where R^{20} and R^{21} which may be the same or different are as defined above for R^{20} and m and n are integers and for each m or n greater than 1 each R^{20} and R^{21} may be the same or different. Examples of such phenols include 2,2'-dihydroxy-5,5'-dimethyldiphenylmethane; 5,5'-dihydroxy-2,2'-dimethyldiphenylmethane; 4,4'-dihydroxy-2,2'-dimethyl-dimethyldiphenylmethane ; 2,2'-dihydroxy-5,5'-dinonyldiphenylmethane; 2,2'-dihydroxy-5,5'-didodecylphenylmethane; 2,2',4,4'-tetra-t-butyl-3,3'-dihydroxy-5,5'-didodecylphenylmethane; and 2,2',4,4'-tetra-t-butyl-3,3'-dihydroxydiphenylmethane.

Also included are sulphurized phenols of the formula:



and/or

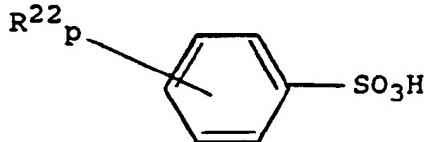


where R^{20} and R^{21} which may be the same or different are as defined above, and m and n are integers, for each m and n greater than 1 each R^{20} and R^{21} may be the same or different, and x is 1,2,3 or 4. Examples of such phenols include:

2,2'-dihydroxy-5,5'-dimethyldiphenylsulphide;
5,5'-dihydroxy-2,2'-di-t-butyldiphenyldisulphide;
4,4'-dihydroxy-3,3'-di-t-butyldiphenylsulphide;
2,2'-dihydroxy-5,5'-dinonyldiphenyldisulphide;
2,2'-dihydroxy-5,5'-didodecyldiphenyldisulphide;
2,2'-dihydroxy-5,5'-didodecyldiphenyltrisulphide; and
2,2'-dihydroxy-5,5'-didodecyldiphenyltetrasulphide.

The sulphonic acids from which the anion may be derived include alkyl and aryl sulphonic acids which have a total of 1 to 200 carbon atoms per molecule although the preferred range is 10 to 80 atoms per molecule.

Included in this description are aryl sulphonic acids of the formula:



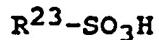
where $p = 1, 2, 3, 4, 5$ and when $p > 1$ the substituents may be the same or different, and R^{22} may represent R^{20} as defined above.

The hydrocarbon group(s) may be bonded to the benzene ring through a carbonyl group or a thio-keto

group. Alternatively the hydrocarbon group(s) may be bonded to the benzene ring through a sulphur, oxygen or nitrogen atom. Thus examples of sulphonic acids that may be used include: benzene sulphonic acid; o-toluene-sulphonic acid, m-toluenesulphonic acid; p-toluene-sulphonic acid; 2,3-dimethylbenzenesulphonic acid; 2,4-dimethylbenzenesulphonic acid; 2,3,4-trimethylbenzenesulphonic acid; 4-ethyl-2,3-dimethylbenzenesulphonic acid; 4-ethylbenzenesulphonic acid; 4-n-propylbenzenesulphonic acid; 4-n-butylbenzenesulphonic acid; 4-isobutylbenzenesulphonic acid; 4-sec-butylbenzenesulphonic acid; 4-t-butylbenzenesulphonic acid; 4-nonylbenzenesulphonic acid; 2-dodecylbenzenesulphonic acid; 4-dodecylbenzenesulphonic acid; 4-cyclohexylbenzenesulphonic acid; 2-cyclohexylbenzenesulphonic acid; 2-allylbenzenesulphonic acid; 2-phenylbenzenesulphonic acid; 4(4'-methylphenyl)benzenesulphonic acid; 4-methylmercaptobenzenesulphonic acid; 2-methoxybenzene sulphonic acid; 4-phenoxybenzenesulphonic acid; 4-methylaminobenzenesulphonic acid; 2-dimethylaminobenzenesulphonic acid; and 2-phenylaminobenzenesulphonic acid. Also included are

sulphonic acids of the type listed above where R²² is derived from the polymerization of a low molecular weight olefin e.g. polypropylenebenzenesulphonic acid and polyisobutylenebenzenesulphonic acid.

Also included are sulphonic acids of the formula:



where R²³ is substituted or unsubstituted alkyl, cycloalkyl, alkenyl or cycloalkenyl. Examples of such sulphonic acids that may be used include methylsulphonic acid; ethylsulphonic acid; n-propylsulphonic acid; n-butylsulphonic acid; isobutylsulphonic acid; sec-butylsulphonic acid; t-butylsulphonic; nonylsulphonic acid; dodecylsulphonic acid; polypropylsulphonic acid; polyisobutylsulphonic acid; cyclohexylsulphonic acid; and 4-methylcyclohexylsulphonic acid.

As indicated above, each category of compound (a), (b), and (c), may be represented by one or more compounds of one or more metals. The compound or compounds may be "neutral", i.e., in which the metal is combined with a stoichiometric quantity of the acid, or may be "over-based", i.e., in which the metal is present in excess, part of the metal being present in the form of an oxide, hydroxide, sulphide, sulphite, sulphate, nitrite, nitrate, phosphite, phosphate or, preferably, carbonate.

Each category of metal compound is advantageously present in the additive in a proportion such that, when

added to a fuel oil, the content of each metal is within the range of 1 to 10000 ppm, more advantageously 5 to 1000, and preferably 5 to 100 ppm, the total proportion of metal being then 3 to 30000, 15 to 3000 and 15 to 300 ppm in the fuel oil.

Although we do not wish to be bound by any theoretical explanations, it is believed that alkali metal compounds positively charge any soot platelets that form during combustion, and reduce the ignition temperature of soot. Positively charged platelets would not agglomerate so quickly as uncharged platelets, and with a greater surface area exposed would oxidize more quickly. Group 2a metals are believed to generate hydroxyl radicals that are reactive in oxidizing the soot nuclei that would otherwise grow to the platelets; transition metals are believed to catalyse soot oxidation.

In the case of diesel and jet engines, wherein a small part of the lubricating oil is burnt along with the fuel, the additive may be incorporated in the lubricating oil.

The present invention also provides a fuel oil or lubricating oil composition comprising oil and the additive.

The invention further provides an oil concentrate comprising the composition in solution in an oil, either a fuel oil or a lubricating oil, or in a solvent miscible with the oil to which the composition is to be added.

The invention still further provides the use as a smoke and/or particulate-reducing additive for, and the use in reducing smoke and/or particulate emission in the combustion of, a fuel oil of the additive composition of the invention.

The following Examples illustrate the invention:

Example 1

A modern six cylinder, four stroke, direct injection diesel engine was used in a series of tests designed to examine the effect of injection timing and a combination of metal additives on black smoke. The engine had a total swept volume of 5958 ml, a maximum power of 100 kW at 2800 rpm, and a maximum torque of 402 Nm at 1400 rpm. The injection timings used were the manufacturer's recommended setting advanced and retarded by up to 5° crankcase angle from the recommended setting. The engine was run at 2800 rpm and 90% of the maximum load.

The fuel used in the experiments in this Example was a conventional European diesel having a cetane number of 50 and a sulphur content of 0.25%. The fuel was treated with three additives:

- (a) A barium carbonate overbased barium sulphonate containing 14.6% barium. This was used at concentrations such that the barium content of the fuel was 0, 50, or 100 ppm.
- (b) A sodium carbonate overbased sodium sulphonate containing 16.6% sodium. This was used at

concentrations such that the barium content of the fuel was 0, 50, or 100 ppm.

- (c) A neutral cobalt carboxylate which contained 10.0% cobalt. This was used at concentrations such that the cobalt content of the fuel was 0, 50, or 100 ppm.

The tests were set up according to a standard statistical design. Each test was run for 30 minutes to allow the engine to stabilize before smoke measurements were recorded. The results of the tests are shown in Table 1.

Analysis of the results shows that the Bosch smoke reaches a minimum of 0.88 when:

- 1) The injection timing is set at -2.2° crankcase angle from the manufacturer's recommended setting.
- 2) The concentration of barium in the fuel is 100 ppm.
- 3) The concentration of sodium in the fuel is 34 ppm.
- 4) The concentration of cobalt in the fuel is 50 ppm.

This compares with a minimum Bosch smoke for the untreated fuel of 1.52, also obtained when the injection timing is set at -2.2° crankcase angle from the manufacturer's recommended setting.

Example 2

The same engine was used as in Example 1, under the same conditions of speed and load. The injection angle was advanced and retarded by up to 4° from the manufacturer's recommended setting. The fuel used was

similar to that used in Example 1 and was treated with:

- (a) A calcium carbonate overbased sulphurized calcium phenate containing 9.5% calcium. (Calcium content of fuel: 0, 100 and 200 ppm.)
- (b) An iron salt of a high molecular weight carboxylic acid containing 10% iron. (Iron content of fuel: 0, 100 and 200 ppm.)
- (c) A neutral potassium sulphonate containing 8% potassium. (Potassium content of fuel: 0, 100 and 200 ppm.)

The tests were set up according to a standard statistical design. In these tests particulates were measured as well as black smoke. Particulate formation is measured by diverting part of the engine exhaust gas into a tunnel, mixing it with air flowing at a known rate and filtering it through a weighed filter paper maintained at 52°C. During the test, the NO_x concentrations of the tunnel gas and the remainder of the exhaust gas were measured to enable, after correcting for temperature differences, the fraction of exhaust passing through the tunnel to be calculated. At the end of the test, the filter paper is weighed again, and the increase divided by the fraction to give the particulate coefficient, in mg/test.

The results are shown in Table 2. Analysis of the results shows that the minimum Bosch smoke is 0.97, which is obtained when:

- 1) The injection timing is set at -4° relative to the manufacturer's recommended setting.
- 2) The concentration of calcium is 200 ppm.
- 3) The concentration of iron is 86 ppm.
- 4) The concentration of potassium is 177 ppm.

The smoke level compares with a minimum of 2.10 for the untreated fuel which is also obtained when the injection timing is set at -4° from the manufacturer's recommended setting.

The minimum for the particulate coefficient is 97 which is obtained when:

- 5) The injection timing is set at -4° relative to the manufacturer's recommended setting.
- 6) The concentration of calcium is 112 ppm.
- 7) The concentration of iron is 173 ppm.
- 8) The concentration of potassium is 0 ppm.

This compares with a minimum particulate coefficient of 235 for the untreated fuel, which is obtained when the injection timing is set at -4° from the manufacturer's recommended setting.

TABLE 1

TEST No.	INJ TIME deg. CA	Br/PPm	Na/PPm	Co/PPm	SMOKE BOSCH CARTRIDGE	SMOKE HARTRIDGE
1	-8.0	50	50	100	1.85	16.2
2	-8.4	50	50	0	1.95	17.2
3	-4.2	0	100	100	3.32	36.0
4	-4.2	100	0	100	2.92	33.1
5	-4.0	100	100	0	3.37	41.8
6	-8.2	50	50	50	1.85	16.2
7	-8.4	50	100	50	1.76	17.2
8	-4.0	100	100	100	2.95	32.4
9	-12.6	50	50	50	1.62	14.2
10	-8.4	50	0	50	1.46	11.8
11	-4.0	0	0	100	3.38	32.1
12	-8.4	50	50	50	1.38	11.8
13	-12.4	100	0	100	1.32	11.1
14	-3.6	0	100	0	3.38	47.2
15	-12.6	0	100	100	1.83	16.7
16	-12.6	100	100	0	1.64	15.7
17	-12.6	100	0	0	1.60	14.8
18	-3.6	0	0	0	3.39	42.7
19	-8.4	50	50	50	1.36	13.2
20	-12.6	0	0	0	1.90	17.0
21	-12.4	0	0	100	1.50	13.0
22	-8.4	0	50	50	1.28	14.2
23	-8.4	50	50	50	1.28	13.2
24	-8.0	100	50	50	1.13	11.1
25	-12.4	0	100	0	2.00	19.0
26	-3.4	100	0	0	3.39	36.9
27	-8.2	50	50	50	1.54	14.2
28	-8.2	50	50	50	1.27	12.1
29	-8.2	50	50	50	1.36	14.2
30	-12.6	100	100	100	1.60	14.6
31	-4.0	50	50	50	3.19	35.9

TABLE 2

EXPT. NO.	C _a (ppm)	F _e (ppm)	K(ppm)	INJ(deg)	SMOKE (BOSCH)	SMOKE (HARTRIDGE)	PART. COEFF.
ED01	0	0	0	-12.2	1.8	17	241
ED02	200	0	200	-12.0	1.0	9	234
ED03	0	0	200	-12.0	2.1	19	314
ED04	200	200	200	-12.0	1.2	11	277
ED05	0	200	200	-12.4	1.8	14	300
ED06	0	200	0	-12.0	1.9	14	153
ED07	200	0	0	-12.0	1.3	10	221
ED08	200	200	0	-12.0	1.7	14	261
ED09	100	100	100	-12.0	1.5	14	292
ED10	100	0	100	-8.2	2.0	19	337
ED11	100	200	100	-8.6	2.0	21	415
ED12	100	100	100	-8.2	2.0	19	366
ED13	100	100	100	-8.4	2.1	19	359
ED14	200	100	100	-8.4	1.6	18	415
ED15	0	100	100	-8.2	2.2	22	427
ED16	100	100	100	-8.4	1.8	17	358
ED17	100	100	200	-8.2	2.1	20	403
ED18	100	100	100	-7.8	1.4	14	232
ED19	100	100	100	-7.8	1.8	17	318
ED20	100	100	0	-8.2	1.5	15	254
ED21	100	100	100	-8.2	1.8	17	302
ED22	100	100	100	-8.0	1.9	19	350
ED23	0	200	200	-4.4	2.8	30	797
ED24	200	0	200	-4.4	2.3	25	659
ED25	0	0	0	-4.4	3.3	35	697
ED26	0	0	200	-4.4	3.4	38	812
ED27	200	200	200	-4.4	2.3	24	719
ED28	0	200	0	-4.2	2.8	27	621
ED29	100	100	100	-4.2	2.2	25	573
ED30	200	200	0	-4.2	2.5	26	595
ED31	200	0	0	-4.0	2.5	29	573

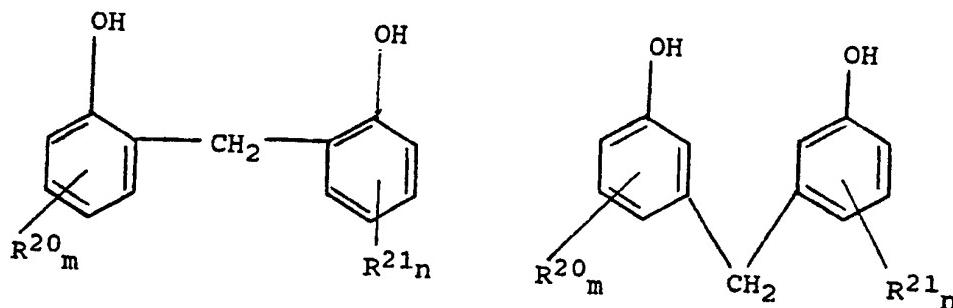
Claims:

1. A composition comprising
 - (a) a compound of an alkali metal,
 - (b) a compound of a metal of group 2a of the Periodic Table, and
 - (c) a compound of a transition metal selected from Groups 1b, 3b, 4b, 5b, 6b, 7b or 8 of the Periodic Table.
2. A composition as claimed in claim 1, wherein the alkali metal is sodium or potassium.
3. A composition as claimed in claim 1 or claim 2, wherein the Group 2a metal is calcium or barium.
4. A composition as claimed in any one of claims 1 to 3, wherein the transition metal is chromium, manganese, iron, cobalt, nickel, copper, or lanthanum.
5. A composition as claimed in any one of claims 1 to 4, which comprises compounds of sodium or potassium, barium or calcium, and cobalt or iron.
6. A composition as claimed in any one of claims 1 to 4, which comprises compounds of sodium, barium and cobalt.
7. A composition as claimed in any one of claims 1 to 4, which comprises compounds of potassium, calcium and iron.
8. A composition as claimed in any one of claims 1 to 7, wherein at least one metal compound is a metal salt of an organic acid.

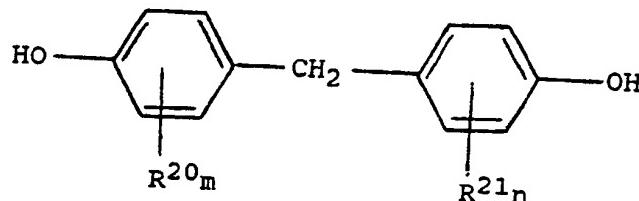
9. A composition as claimed in claim 8, wherein the anion of the salt is derived from a carboxylic acid or a carboxylic acid anhydride.

10. A composition according to claim 8, wherein the anion of the salt is derived from a phenol, a sulphurized phenol, or a sulphonate acid.

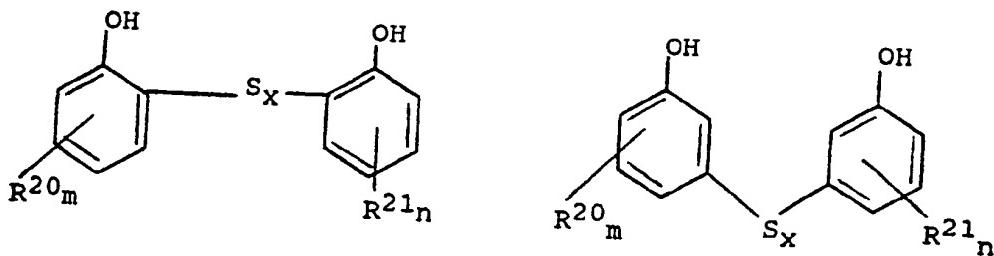
11. A composition according to claim 8, wherein the anion of the salt is derived from a methylene bis-phenol of the formula:



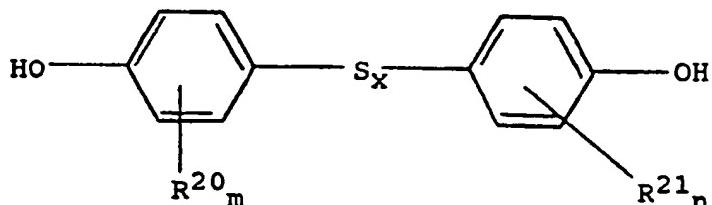
or



or a sulphurized phenol of the formula:

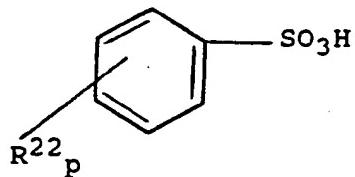


or



where R^{20} and R^{21} which may be the same or different are hydrogen, or a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, cycloalkenyl, or aryl group, m and n which may be the same or different are each zero or an integer from 1 to 4 and for each m or n greater than 1 each R^{20} or R^{21} may be the same or different, and x is 1, 2, 3 or 4.

12. A composition according to claim 8, wherein the anion of the salt is derived from a sulphonic acid of the formula:



where R^{22} is hydrogen, or a substituted or unsubstituted alkyl, cycloalkyl, alkenyl, cycloalkenyl, or aryl group, p is an integer of 1 to 5 and when p is greater than 1 each R^{22} may be the same or different.

13. A composition as claimed in claim 8, wherein the cation and the anion are present in stoichiometric proportions.

14. A composition as claimed in claim 8, wherein the salt is an overbased salt.

15. A composition as claimed in claim 1, substantially as described in either of the Examples herein.

16. An oil composition, which comprises a diesel oil, jet fuel, heating oil or lubricating oil, and an additive composition as claimed in any one of claims 1 to 15.

17. A composition as claimed in claim 16, wherein each of component (a), (b), and (c) is present in a proportion of 1 to 10000 ppm.

18. A composition as claimed in claim 16, wherein the additive composition is present in a proportion of 3 to 30000 ppm.

19. A composition as claimed in claim 17, wherein the proportion is from 15 to 3000 ppm.

20. A composition as claimed in claim 17, wherein the proportion is from 15 to 300 ppm.

21. An additive concentrate comprising a composition as claimed in any one of claims 1 to 15 in an oil solution or in a solvent miscible with oil.

22. Use of a composition as claimed in any one of claims 1 to 15 to reduce smoke and/or particulate emission in the combustion of a fuel oil.

23. Use of a composition as claimed in any one

of claims 1 to 15 as a smoke and/or particulate emission inhibiting additive in a fuel oil.

24. Any new feature hereinbefore described or any new combination of hereinbefore described features.

THIS PAGE BLANK (USPTO)